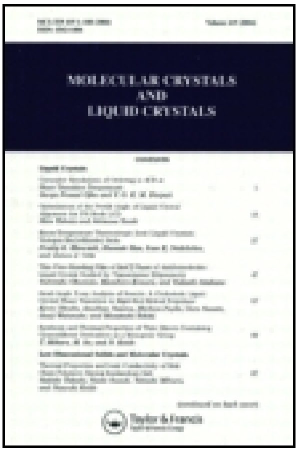

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Fabrications and Optical Properties of Phthalocyanine Multi-Layered Films

Yasuo Imanishi [a], Shintarou Hattori [a], Tomoyuki Hamada [a], Shingo Ishihara [a], Atsushi Kakuta [a] & Shunichi Numata [a]
[a] Hitachi Research Laboratory, Hitachi Ltd., 7-1-1, Ohmika-cho, Hitachi-shi, Ibaraki-ken, 319-12, JAPAN

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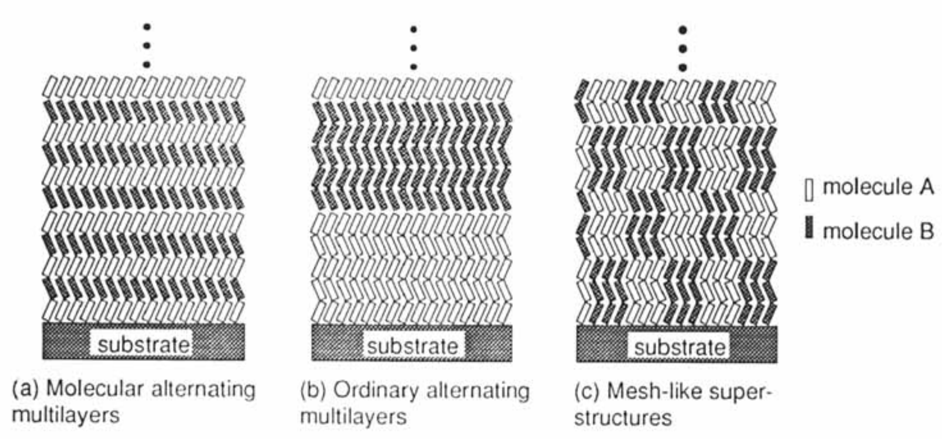
FABRICATIONS AND OPTICAL PROPERTIES OF PHTHALOCYANINE MULTI-LAYERED FILMS

YASUO IMANISHI, SHINTAROU HATTORI, TOMOYUKI HAMADA,
SHINGO ISHIHARA, ATSUSHI KAKUTA, AND SHUNICHI NUMATA
Hitachi Research Laboratory, Hitachi Ltd., 7-1-1,
Ohmika-cho, Hitachi-shi, Ibaraki-ken, 319-12 JAPAN

Abstract Phthalocyanine multi-layered films, composed of copper phthalocyanine (CuPc) and naphthalene tetracarboxylic dianhydride (NTCDA), were fabricated by an organic molecular beam deposition method. Results from several analyses, like XPS and RHEED, revealed an epitaxial layer-by-layer structure of the multilayers, pointing toward a possible candidate of molecular assembly for future photonics devices.

INTRODUCTION

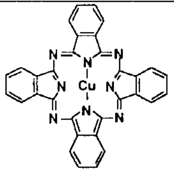
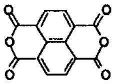
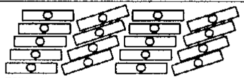
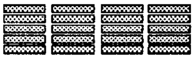
Organic superlattice (OSL) structures, consisting of multi-layered ultra-thin films of different organic molecules, are expected to provide a new molecular assembly and unique properties, especially applicable to advanced optical and electronic devices, and differing from conventional semiconductor superlattices. It is easy to draw schematic pictures of organic superlattices with molecular or ordinary alternating multilayers, or mesh-like superstructures (figure 1). However, it is very difficult and complicated to construct these OSL structures from any kind of organic molecules, even though electronic states of organic crystals for the photonics are mainly dominated by their components, chemical structures, their aggregate structures, and interactions between molecules. Development of a fabrication process for organic ultra-thin films by means of an organic molecular beam deposition (OMBD) technique has made it dream possible to construct a complicated molecular as-



(a) Molecular alternating multilayers (b) Ordinary alternating multilayers (c) Mesh-like super-structures

Fig. 1 Models of organic superlattices.

Table 1 Characteristics of CuPc and NTCDA single crystals.

compound	CuPc (α-form)	NTCDA
molecular formula	$CuC_{32}H_{16}N_8$	$C_{14}H_4O_6$
crystal symmetry	monoclinic	monoclinic
space group	C2/c	$P2/c_1$
a(Å)	25.92	7.867(2)
b(Å)	3.790	5.305(1)
c(Å)	23.92	12.574(2)
β(°)	90.4	72.73(2)
Z	4	2
structural formula		
stacking habit		
stacking angle (°)	0, 20	0
molecular spacing (Å)	3.38	3.506

sembly in which higher crystallinity and a smoother surface than gotten by ordinary vapor deposition are achieved [1-4].

In particular, three groups have been worked on the fabrication of organic multi-layered thin films. So *et al.* [5] formed multilayers composed of perylene and naphthalene derivatives (PTCDA/NTCDA) on quartz glass substrates. Tada *et al.* [6] identified the hetero epitaxial growth of phthalocyanine derivatives (VOPc/AlClPc) on several kinds of alkali halide substrates. Nonaka, *et al.* [7] reported the fabrication and identification of multilayered films of porphyrin derivatives (H_2TPP/ZnTPP) on the hydrogen terminated surface of silicon. These findings have led us to believe it is possible to intentionally design an electronic structure in OSL structures with a variety of chemical structures and electronic states, which may lead to new developments in optical or electrical devices.

The final target of our work is the realization of nonlinear optical devices, especially for ultrafast optical switching. For such a purpose large nonlinear optical suscept-ibilities may be attained in the OSL system due to exciton confinement in a low dimensional system, like ZnSe supermicro particles, the GaAs/GaAlAs semiconductor superlattice, and the crystal surface of anthacene [8]. Our aims in the first stage are to determine whether we can fabricate superlattice structures with organic molecules having no alkyl chain group for the Langmuir-Blodgett films and to identify the modifications of electronic states in new molecular assemblies which are suited for nonlinear optical devices.

In this paper we make a brief review of our recent study [9] and its further results on the multi-layered ultra-thin films of copper phthalocyanine (CuPc) and naphthalene-1,4,5,8-tetra-carboxylic-1,8:4,5-dianhydride (NTCDA) by OMBD. We show a stacking model of the multilayers developed from results of several structure analyses for the films.

EXPERIMENTALS

The details of our OMBD fabrications have already been given elsewhere [9, 10]. The typical base pressure of the OMBD apparatus was on the order of 10^{-10} Torr. CuPc and NTCDA were commercially obtained from Tokyo Chemical Industry Co., Ltd., and purified by sublimation before use. The potassium chloride substrates (KCl), polished at the (100) surface , were used after heating at 400 °C for 8h in the OMBD apparatus. The substrate temperatures were kept at -50°C (calibrated). The growth rates and thicknesses of the films were monitored by quartz vibrators. Typical growth rates were 0.5nm/h for CuPc and 2nm/h for NTCDA. The film structures were analyzed by reflection high energy electron diffraction (RHEED) and X-ray photoelectron spectroscopy (XPS) in the analysis chamber and by transmission electron microscopy (TEM) externally.

RESULTS AND DISCUSSIONS

Table 1 lists the characteristics of these single crystals [11, 12]. Both are planar π-conjugated molecules with columnar stacking. These two compounds are organic semiconductors with quite different band gaps; in particular, NTCDA acts as a molecular electron acceptor to many organic compounds [13]. If we can fabricate superlattice structures of these compounds, then not only exciton confinements in one kind of molecular layer but also charge transfers induced at the the interfaces of each layers are possible. The CuPc crystals have two stacking angles, 0 and 20°, while NTCDA crystals have the 0° angle only. So when a multilayer structure is formed by

MBD, control of molecular orientations in each layer can give heteroepitaxial growth.

So at first CuPc was deposited on the KCl(100) surface. Prior research [11] on CuPc vapor deposition revealed there was cofacial anchoring of CuPc molecules, in which the copper cation of CuPc and the chlorine anion of the substrate affected each other, and the bridging nitrogen of CuPc and the potassium cation could also affected. Figure 2 shows the RHEED pattern of the CuPc layer on a KCl(100) substrate. In the center of the view, five weak streaks could be recognized and their distance between the streaks corresponded to the 1.3 to 1.4 nm lattice distance in the surface structure of the films. This confirmed the cofacial adsorption of CuPc.

The deposition order of the multilayers was as follows: the first layer was CuPc, the second NTCDA, the third CuPc, and so on, finishing with a CuPc top layer and the total number of layers of eleven. Due to the difference in vapor pressures of CuPc and NTCDA, a relatively low substrate temperature was selected for fabrication of the multilayers. At such a low temperature, the marginal migration of deposited species on the substrates was expected to occur.

Figure 3 shows the *in situ* XPS spectra of the multilayers, in which monitored thicknesses were (a) 20Å and (b) 50Å per layer. For the 50Å thickness, three signals, $Cu2p_{1/2}$, $Cu2p_{3/2}$, and N1s, which stemmed from the CuPc molecule, and one signal, O1s, from the NTCDA molecule, appeared in alternate layers, meanwhile for the 20Å thickness there were residual signals from the sublayer. These facts gave indirect evidence for the layer-by-layer structure of these films.

Figure 4 shows the TEM surface view and the electron diffraction pattern for the CuPc and NTCDA multilayers (50Å per layer). On the surface there were lattice images of CuPc crystals (parallel straight lines with ca. 13Å pitch) and the size of each crystal domain was about 500Å.

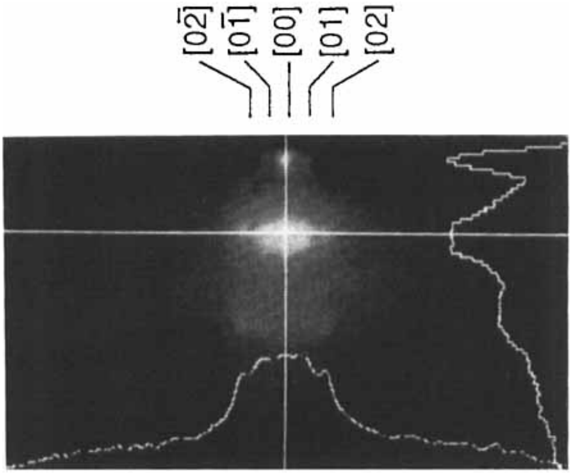
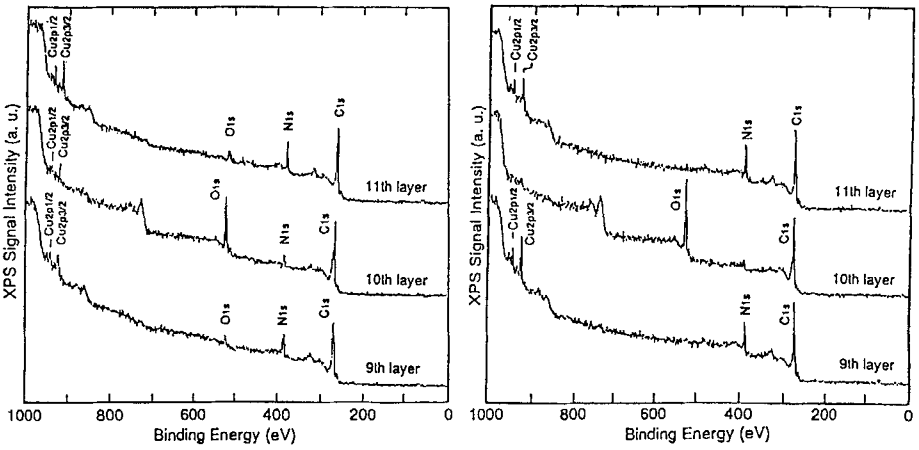


Fig. 2 RHEED pattern of the CuPc layer on a KCl (100) substrate.



(a) 20Å per one layer

(b) 50Å per one layer

Fig. 3 XPS spectra of the CuPc and NTCDA multilayers on a KCl substrate.

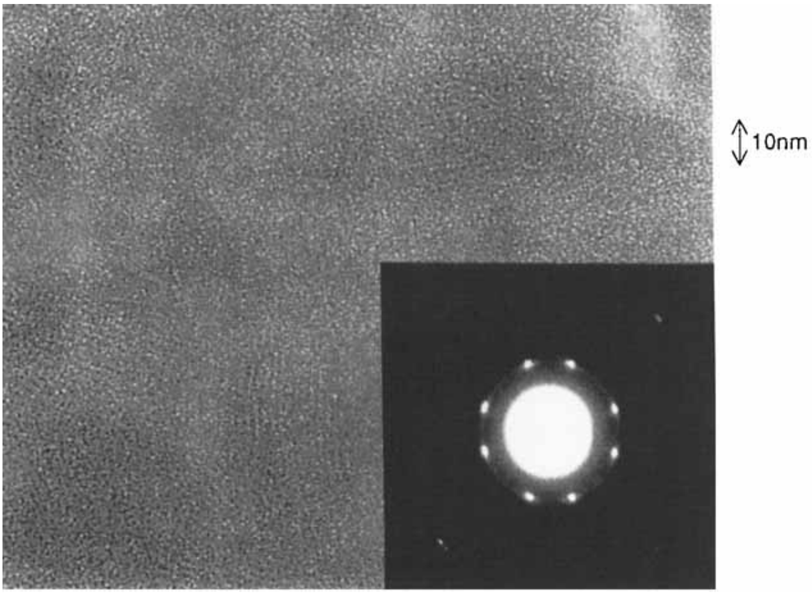


Fig. 4 The TEM surface view and the electron diffraction pattern (intersection) for the CuPc and NTCDA multilayers (50Å per one layer).

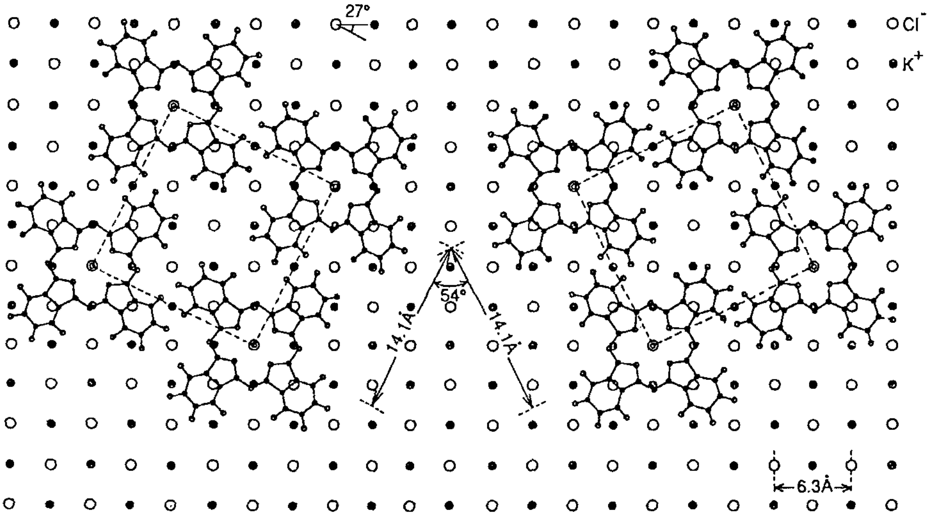


Fig. 5 Possible arrangements of CuPc molecules on a KCl(100) surface (√5×√5±27°).

The diffraction pattern could be analyzed as an overlap of two types of arrangements of CuPc molecules on the KCl substrate (Figure 5) and a heteroepitaxial structure retaining the symmetry of the first layer.

Figure 6 shows a TEM cross sectional photograph of the multilayers with a 50Å thickness per layer (monitored). We clearly observed a layer-by-layer structure, in which the CuPc appeared as a dark layer and the NTCDA as a light one, owing to their different constituent elements, and the number of layers coincided with the established one. The thickness of one layer was 1 to 2nm. There was some thickness deviation between layers due to changes in the molecular beam density, due to stopping the deposition to carry out the layer analysis. Total thickness was ca. 15nm. Therefore, formation of the OSL structure, composed of multilayered ultra-thin films of different organic molecules, was confirmed as being a few nanometers thickness.

Figure 7 shows one possible stacking model of the multilayer. The CuPc molecules were adsorbed on the KCl(100) surface epitaxially. Even though we have no evidence giving a molecular orientation for NTCDA, the stacking structure of NTCDA single crystals could be applied to the multilayers. Here we postulate the preservation of the first layer surface symmetry by the second layer. The third layer might grow like the first layer and so on. Such layer growth would retain the total symmetry initiated in the first layer. At present we are trying to identify such a model by other analysis methods.

From these results, we concluded that multilayers of CuPc and NTCDA, with a few nanometers thickness, were indeed fabricated by the OMBD method. They were confirmed by direct TEM observation of the surface and cross section structure. Proper combinations of layer species and further thermal treatments of deposited films may offer other OSL structures.

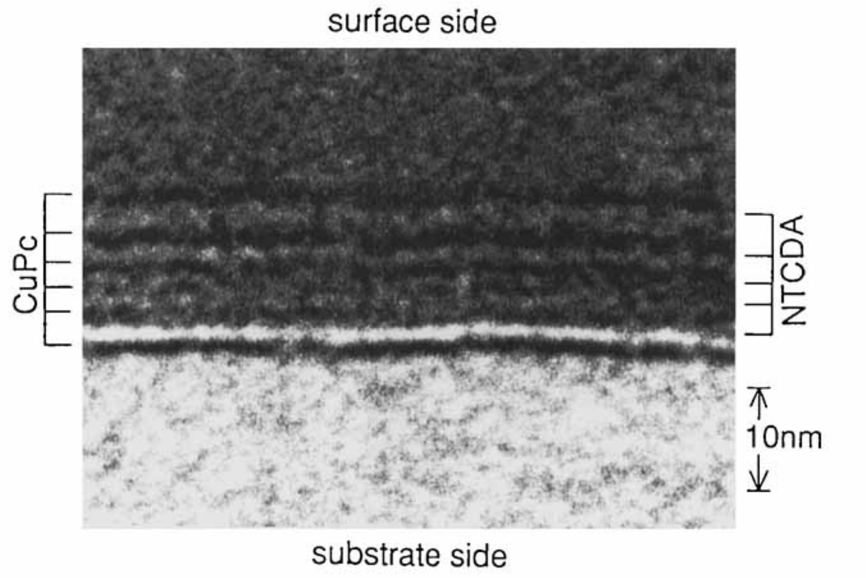


Fig. 6 The TEM sectional view of the CuPc and NTCDA multilayers.

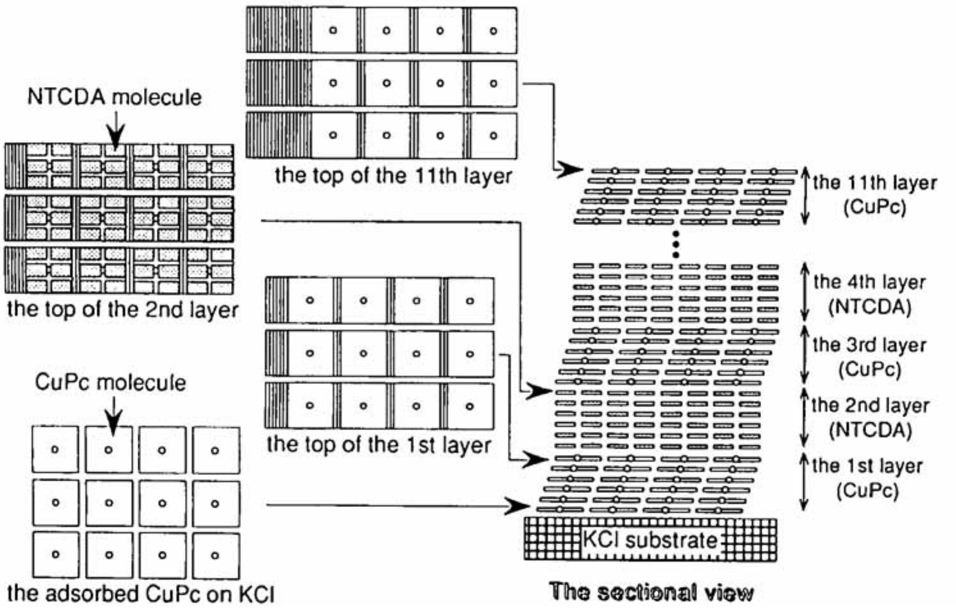


Fig. 7 The stacking model of the multilayer.

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